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6. AUTHOR(S) Dr Hilary L. Lackritz				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) School of Chemical Engineering Purdue University West Lafayette IN 47907-1283			AFOSR-TR-96 0470	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) AFOSR/NL 110 Duncan Ave Room B115 Bolling AFB DC 20332-8080 Dr Charles Y-C. Lee			10. SPONSORING / MONITORING AGENCY REPORT NUMBER	
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13. ABSTRACT (Maximum 200 words) The goals of the research are two fold; First, determine the internal electric field effects from studies of charge magnitude, symmetry and distribution in dye-doped polymer systems. Second, a better understanding of the electric field effects on the chromophore mobility during and after poling. To this end, several techniques are being employed. Electrochromism technique is being used to determine the charge magnitude inside film samples. The films are 4-dimethylamino-4'-nitrostilbene and disperse red 1 chromophores doped into poly(Methyl methacrylate) guest-host systems. Charge symmetry is also being studies using thermal pulse experiments. Preliminary result show that the charges are distributed linearly in the sample. More tests will be performed in search of any local charge distribution inhomogeneities. An interferometric technique with in-situ poling was used to probe the poling field-induced molecular alignment of the chromophores as a function of temperature. Results are showing the dependence of poling on electric fields (magnitude and polarity). Integrated systems will further reveal the loses in the films due to the field dependent chromophore orientation.				
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Program Manager: Dr. Charles Lee

"Electric Field Effects in Polymer Thin Films for Second Order Nonlinear Optical Applications".

Hilary S. Lackritz
School of Chemical Engineering
Purdue University
West Lafayette, Indiana 47907-1283

phone: (317) 494-4065
fax: (317) 494-0805
login: lackritz@ecn.purdue.edu

September 1, 1996

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SUMMARY OF PROGRESS year 3

Status

The goals of the research are two fold; First, determine the internal electric field effects from studies of charge magnitude, symmetry and distribution in dye-doped polymer systems. Second, a better understanding of the electric field effects on the chromophore mobility during and after poling. To this end, several techniques are being employed. Electrochromism technique is being used to determine the charge magnitude inside film samples. The films are 4-dimethylamino-4'-nitrostilbene and disperse red 1 chromophores doped into poly(methyl methacrylate) guest-host systems. Charge symmetry is also being studied using thermal pulse experiments. Preliminary results show that the charges are distributed linearly in the sample. More tests will be performed in search of any local charge distribution inhomogeneities. An interferometric technique with *in-situ* poling was used to probe the poling field-induced molecular alignment of the chromophores as a function of temperature. Results are showing the dependence of poling on electric fields (magnitude and polarity). Integrated systems will further reveal the losses in the films due to the field dependent chromophore orientation.

RESEARCH OBJECTIVES

The challenge of understanding electric field effects on polymer has been pursued by other researchers. Most research has been focused on conditions of electric field induced breakdown or on bulk polymer samples. However, thin polymer films are being used in the presence of high sub-breakdown electric fields for photonic applications as well as for coatings and insulators. Our **primary research objective** is to determine the electric field effects on these polymer thin film systems for second order nonlinear optical applications.

1) Charge magnitude, symmetry and distribution across a polymer thin film will be determined. At temperatures above the glass transition temperature of the polymer system where poling usually occurs, there is significant charge injection into the polymer film. This injected charge can influence the electric field sensed by the chromophores throughout the polymer film. It is imperative to understand the charge distribution through the polymer film in order to optimize poling procedures. Therefore, the charge magnitude, symmetry and distribution will be determined as a function of time, temperature, thickness, poling and concentration of dopant using the techniques of electrochromism and thermal pulse measurements.

2) The electric field effects on the rotational mobility of chromophores in polymer thin film systems will be determined. The rotational mobility of the chromophores in the polymer depends strongly on the electrical field sensed by the chromophores which may differ from the applied electrical field. The rotational mobility will be determined using dielectric relaxation and second order nonlinear optics. These techniques will be used to study the thermal and temporal stability of the chromophore orientation.

AFOSR Grant/Contract Summary

PI Name: Hilary S. Lackritz

Institution: Purdue University, School of Chemical Engineering

- (1) Number of PI involved: 1
- (2) Number of Post-Doc Supported: 1
- (3) Number of Graduate Students Supported: 2
- (4) Other researchers supported: 1
- (5) Number of Publications: 8
- (6) Number of Publications- AFOSR support: 3
- (7) Awards and Honors Received by the PI (lifetime): see attached

- (1) Number of PI involved: 1 Hilary S. Lackritz

(2) Number of Post-Doc Supported: 1

Dr. Fassil Ghebremichael: until 7/96- currently at Assistant Professor, USAF Academy, Colorado Springs, Department of Physics.

(3) Number of Graduate Students Supported: 2

Mr. Mark Ostrowski: plans on finishing Ph.D. 12/96

Mr. Seung-Jin Lee: second year graduate student at Purdue (MS degree, KAIST)

(4) Other researchers supported: 1

Dr. Ken Haber, Department of Chemistry laser facility

(5) Number of Publications: 8

Lackritz, H.S.; Liu, L.-Y.; Wright, M.E.; Mullick, S. "Study of Poling and Relaxation in Kink and Linear Main-Chain Functionalized Polymers for Second Order Nonlinear Optical Applications" *Macromolecules*, 1995, 28, 1912.

*Pasmore, T.; Talbot, J.; Lackritz, H. S. "Monte-Carlo Simulations of Electric Field Hopping in Doped Polymer Thin Films" *Mol. Cryst. Liq. Cryst. Sci. Tech. B: Nonlinear Optics*, 1995, 10, 295.

Zhuang, X.; Lackritz, H.S.; Shen, Y.R. "Photo-isomerization of Polymer Monolayers and Multilayers on Water" *Chem. Phys. Lett.*, 1995, 246, 279-284.

Fu, C.Y.S.; Lackritz, H.S.; Priddy, D. B. Jr.; McGrath, J.E. "Polymer Physics and Structure/Property Relationships of Thermally Stable Polyarylene Ethers for Second Order Nonlinear Optics" *Chem. Mater.*, 1996, 8, 514-524.

Wright, M. E.; Toplikar, E. G.; Lackritz, H. S.; Subramanyan, S. "A Preliminary Study of Poly(p-phenylene) Based NLO Materials" *Chem. Mater.*, 1996, 5, 345.

Fu, C.Y.S.; Lackritz, H.S.; Priddy, D. B. Jr.; McGrath, J.E. "Effects of Chromophore Functionalization and Physical Aging during Poling on Chromophore Orientational Dynamics in Polyarylene Ethers for Second Order Nonlinear Optics" *Macromolecules*, in press.

*Ghebremichael, F.; Kuzyk, M.; Lackritz, H.S. ""Nonlinear Optics and Polymer Physics" *Progress in Polymer Science*, accepted for publication. INVITED REVIEW ARTICLE (28 figures and 263 references).

*Ghebremichael, F.; Lackritz, H.S. "Linear Electro-optic Effects of Dye-Doped Polymers: Temperature and Poling Field Dependencies" *Applied Optics*, accepted for publication.

(6) Number of Publications- AFOSR support: 3

Those marked with an * above

two publications by Mr. Ostrowski are in the process of being submitted at this time.

(7) Awards and Honors Received by the PI (lifetime):

AWARDS AND HONORS

Presidential Faculty Fellows Award (National Science Foundation) 1993-1998

Office of Naval Research Young Investigator Award 1992-1995

Chemical Engineering and all-Engineering Nominee for the Murphy Award for Outstanding Undergraduate Teaching at Purdue University 1994

Shreve Award for Outstanding Undergraduate Teaching, Second Place, Chemical Engineering, 1994, 1995, 1996

Leader-on-Loan (New York State) for the American Association of University Women 1990-1991

Graduate Fellowships and Awards

Dr. Judith Resnick American Fellowship, American Association of University Women Educational Foundation Selected Professions Fellowship 1989-1990

Sigma Xi, Scientific Research Society

Society of Photo-Optical Instrumentation Engineers Scholarship in Optical Engineering 1989

Materials Research Society Graduate Student Award 1989

IBM Graduate Fellowship 1988-1989

John E. Hilliard Symposium (Northwestern University) First Place 1989

Society for the Advancement of Material and Process Engineering 1988 International Graduate Student Awards Competition-Third Place

Walter P. Murphy Fellowship (Northwestern University) 1985-1986

Invited Presentations (presentations indicated by a * funded by this grant):

Lackritz, H. S. "Polymer Physics Studied Using Second Order Nonlinear Optics" presented at the University of Nebraska, Department of Mechanical and Materials Engineering, Lincoln, NE, February 1995.

*Sullivan, L.; Lackritz, H. S. "Characteristic Relaxation Times in Polymers Studied by Nonlinear Optics, Dielectric Relaxation, and Dynamic Mechanical Analysis" presented at Wright-Patterson Air Force Base in Dayton, OH, April, 1995.

Lackritz, H. S. "Polymer Physics Studied Using Second Order Nonlinear Optics" presented at the Massachusetts Institute of Technology, Polymer Seminar Series, Cambridge, MA, May 1995.

Lackritz, H. S. "Polymer Physics Studied Using Second Order Nonlinear Optical Applications" presented at Hercules, Incorporated, Wilmington, DE, June 1995.

*Lackritz, H. S. "Design and Development of Polymers for Second Order Nonlinear Optics" presented at Kyoto Institute of Technology, Kyoto, Japan, July 1995 (Invited Lectureship).

*Liu, L. Y.; Lackritz, H. S. "Polymer Relaxations and Electric Field Effects in Polymers for Second Order Nonlinear Optics" presented at the International Conference on Organic Nonlinear Optics in Gunma, Japan, July 1995.

*Lackritz, H. S.; Sullivan, L. "Polymer Physics and Electric Field Effects in Poled Polymers for Second Order Nonlinear Optics" presented at the International Conference on Advanced Materials, International Union of Materials Research Societies, Cancun, Mexico, August 1995.

Lackritz, H. S. "Second Order Nonlinear Optical Polymer Dynamics" presented at Miami University, Materials Science Program, Cincinnati, OH, September, 1995.

Lackritz, H. S. "The Characterization of Polymer Dynamics in Poled Second Order Nonlinear Optical Polymers" presented at the Pacific Polymer Conference, Kauai, HI, December 1995.

Lackritz, H. S. "The Characterization of Polymer Dynamics in Poled Second Order Nonlinear Optical Polymers" presented at Princeton University, Department of Chemical Engineering, Princeton, NJ, January 1996.

Lackritz, H. S. "Polymer Physics and Electric Field Effects in Poled Polymers for Second Order Nonlinear Optics" presented at Notre Dame University, Department of Chemical Engineering, South Bend, IN, January 1996.

Lackritz, H. S. "Optical Characterization of Polymer Dynamics" presented at Northwestern University, Department of Chemical Engineering, Evanston, IL, February 1996.

*Lackritz, H. S.; Ma, J. "Electric Field Effects in Electro-optic Polyimides" presented at Wright-Patterson Air Force Base, Dayton, OH, February 1996.

*Lackritz, H. S.; Ostrowski, M. H. "Electric Field Effects in Polymer Thin Films for Second Order Nonlinear Optical Applications" presented at Antec 96, Society of Plastics Engineers, Indianapolis, IN, May 1996.

Lackritz, H. S. "Structural Relaxation in Polymers for Second Order Nonlinear Optics" to be presented at the International Conference on Organic Nonlinear Optics 3, Marcos Island, FL, December 1996.

Contributed Presentations:

*Ostrowski, M.; Haber, K.; Lackritz, H. S. "Electric Field Effects in Polymer Thin Films Studied Using Electrochromism, Dielectric Relaxation and Second Order Nonlinear Optics" poster presented at the American Physical Society national meeting in San Jose, CA, March 1995.

*Ghebremichael, F.; Lackritz, H. S. "Electro-optic and Second Harmonic Generation Studies of Dye-Doped Thin Film Polymers" presented at the American Physical Society national meeting in San Jose, CA, March 1995.

Subramanyan, S.; Chen, F.; Lackritz, H.S. "Kinetic Studies of Photopolymerization at Metal Surfaces Using Surface Second Harmonic Generation" poster presented at the American Physical Society national meeting in San Jose, CA, March 1995.

*Pasmore, T. A.; Talbot, J.; Lackritz, H. S. "Charge Transport through Chromophore Doped Polymer Thin Films for Second Order Nonlinear Optics" poster presented at the American Physical Society national meeting in San Jose, CA, March 1995.

*Sullivan, L. A.; Lackritz, H. S. "Dynamic Mechanical Analysis and Dielectric Relaxation for Electro-Optical Polymer Applications" presented at the Materials Research Society national meeting in San Francisco, CA, April 1995.

Chen, F.; Subrahmanyam, S.; Lackritz, H. S. "Gas Phase Photopolymerization of Vinyl Monomers on Metallic Substrates Studied Using Surface Second Harmonic Generation" presented at the Materials Research Society national meeting in San Francisco, CA, April 1995.

*Ostrowski, M.H.; Lackritz, H.S. "Electric Field Effects in Poled Polymer Thin Films" presented at the American Chemical Society/Optical Society of America Symposium on Organic Films for Photonic Applications (at OSA national meeting) in Portland, OR, September 1995.

*Ghebremichael, F.; Lackritz, H.S. "Electro-optic and Second Harmonic Generation Studies of Dye-Doped Polymers" presented at the American Chemical Society/Optical Society of America Symposium on Organic Films for Photonic Applications (at OSA national meeting) in Portland, OR, September 1995.

Chen, F.; Subrahmanyam, S.; *Lackritz, H.S. "Studies of Photopolymerization at Metal Surfaces" presented at the American Chemical Society/Optical Society of America Symposium on Organic Films for Photonic Applications (at OSA national meeting) in Portland, OR, September 1995.

*Pasmore, T.A.; Talbot, J.; Lackritz, H.S. "Charge Transport through Polymer Thin Films for Second Order Nonlinear Optics" poster presented at the IEEE Conference on Electrical Insulation and Dielectric Phenomena, Virginia Beach, VA, October 1995.

*Ma, Z.; Lackritz, H. S.; Ermer, S.; Girton, D. G. "Thermal Stability Studies of DCM-Polyimide System for Second-Order Nonlinear Optical Applications" poster presented at the American Physical Society national meeting in St. Louis, MO, March 1996.

*Pasmore, T. A.; Talbot, J.; Lackritz, H. S. "Steady State Charge Transport through Molecularly Doped Polymer Thin Films for Second Order Nonlinear Optics" presented at the American Physical Society national meeting in St. Louis, MO, March 1996.

Chen, F. C.; Lackritz, H.S. "Vapor Phase Photopolymerization of Acrolein on Metallic Substrates" poster presented at the American Physical Society national meeting in St. Louis, MO, March 1996.

*Ostrowski, M.H.; Lackritz, H.S. "Electric Field Effects in Poled Polymer Thin Film Systems" poster presented at the American Physical Society national meeting in St. Louis, MO, March 1996.

Medvedev, G.; Caruthers, J.M.; Lackritz, H.S. "Theoretical Study of SHG Intensity Decay in Dye -Polymer Systems During Physical Aging" poster presented at the American Physical Society national meeting in St. Louis, MO, March 1996.

Zhuang, X.; Lackritz, H.S.; Shen, Y.R. "Photo-Isomerization of Polymer Monolayers and Multilayers on Water", presented at the American Physical Society national meeting in St. Louis, MO, March 1996.

*Pasmore, T.A.; Talbot, J.; Lackritz, H.S. "Electric Field Effects in Polymer Thin Films for Second Order Nonlinear Optics" poster to be presented at the IEEE Conference on Electrical Insulation and Dielectric Phenomena, San Francisco, CA, November 1996.

EXTERNAL COMMITTEES AND ACTIVITIES

Advisory Committees

American Chemical Society/Optical Society of America (ACS/OSA) Symposium on Organic Thin Films for Photonic Applications:

International Advisory Committee 1994-

ACS POLY Program Chair- 1995 Portland OSA meeting

ACS Program Co-Chair- 1996 Orlando ACS meeting

Symposium Co-Chair- 1997 Long Beach OSA meeting

Symposium Co-Chair, Lead- 1998 Miami Beach ACS meeting

Editorial Service

American Physical Society (Division of High Polymer Physics APS DHPP) Publications Committee (1993-). Publication Committee Chair, 1997

Guest Editor: Journal of Polymer Science: Polymer Physics 1996 APS DHPP Special Issue

NATIONAL CONFERENCES

Session Chair - "Electrically and Optically Active Polymers II," American Physical Society Meeting, March 1995, San Jose, CA.

Session Chair - "Conjugated and Conducting Polymers," American Chemical Society Meeting, August 1995, Chicago, IL

Session Chair - "Polymer Relaxation Dynamics," American Physical Society Meeting, March 1996, St. Louis, MO.

Session Chair - Antec 96, Society of Plastics Engineers, May 1996, Indianapolis, IN.

Electro-optic coefficient of dye doped polymers: Dr. Fassil Ghebremichael

I. INTRODUCTION

In recent years, chromophore-doped polymers have gained considerable attention for nonlinear optical applications including electro-optic devices.¹ These polymeric devices are preferred over their inorganic counterparts for their processability, low-cost, and their potential for the optimization of their properties for high mechanical, thermal, and temporal stabilities.² Several experimental techniques have been developed to characterize the properties of such polymeric materials. Second harmonic generation³ (SHG) and thermal stimulated discharge⁴ (TSD) techniques have been used to study polymer relaxation behavior, including the distribution of relaxation times attributed to the variations in local microenvironments of the polymers.⁵ Dielectric permittivity measurements have also been used to characterize the behavior of dye-doped polymers near the glass transition, including the dependence of the glass transition temperature on chromophore concentration.⁶ The linear electro-optic⁷ (EO) effect has also been used to study the second order susceptibility of these chromophore doped polymers. The glass transition of the polymer system may be defined as the temperature where long-range cooperative mobility of about 10 or more of the repeat units occurs.⁸ Thus, the introduction of dopants or other plasticizers noticeably influences long-range cooperativity, resulting in a decrease in magnitude of the glass transition temperature and an increase in the number of modes of polymer relaxations.⁶ Similarly, the mobility of the side group in poly(methyl methacrylate) (PMMA) is also influenced by the introduction of chromophores into the system. The temperature at which these side groups have increased mobility is defined here as T_g .⁹ The thermal response properties of the polymer system are primarily dictated by the characteristics of its glass transition particularly at higher temperatures. Johari¹⁰, McCrum and Morris¹¹, and Heijboer¹² among others have shown that the behavior of the secondary transition plays a role in the thermal characteristics of the polymer system as well.

I. EXPERIMENT

Temperature and electric field dependent linear electro-optic coefficient of dye-doped polymers is being investigated. The small phase variation due to the index of refraction is studied using a Mach-Zehnder interferometer, Fig. 1. This setup is used to study thin films made from 4% wt. N,N dimethylamino-nitrostilbene (DANS) or 4% wt. disperse red 1 (DR1) and poly(methyl methacrylate) (PMMA) solutions. The phase due to the field modulation is,

$$\phi_{\Omega}(t, T) = \frac{\pi n^3 r_{113}(T)}{\lambda} V_{\Omega}(t)$$

where $V_{\Omega}(t)$ is the modulating voltage at frequency Ω and r is the EO coefficient. Figure 2 shows the field dependence of r . The EO coefficient is related to the molecular orientational alignment. There is also phase variation due to film thickness variation. When the modulation field is applied to a sample, the relative phase of the beam path is modified. The two sources for this phase variation are, one originating from the index of refraction variation, which is the focus of this study. The other from film sample thickness variation. Note: when the thickness is varied the effective field across the film is also varied. This is a second order effect.

In order to study the electro-optic coefficient of the films only, the thickness variation must be eliminated or taken into account after independent determination. We have, therefore modified the standard experimental setup to effectively eliminate the thickness variation from the experiment. This was achieved by modifying the Mach-Zehnder interferometer as shown in Fig. 1. Previous works have had to independently determine the phase variation due to the thickness variation.¹³ With this modified setup, it is possible to scan frequency range from tens of Hertz all the way up to frequencies where the piezoelectric effects are significant.

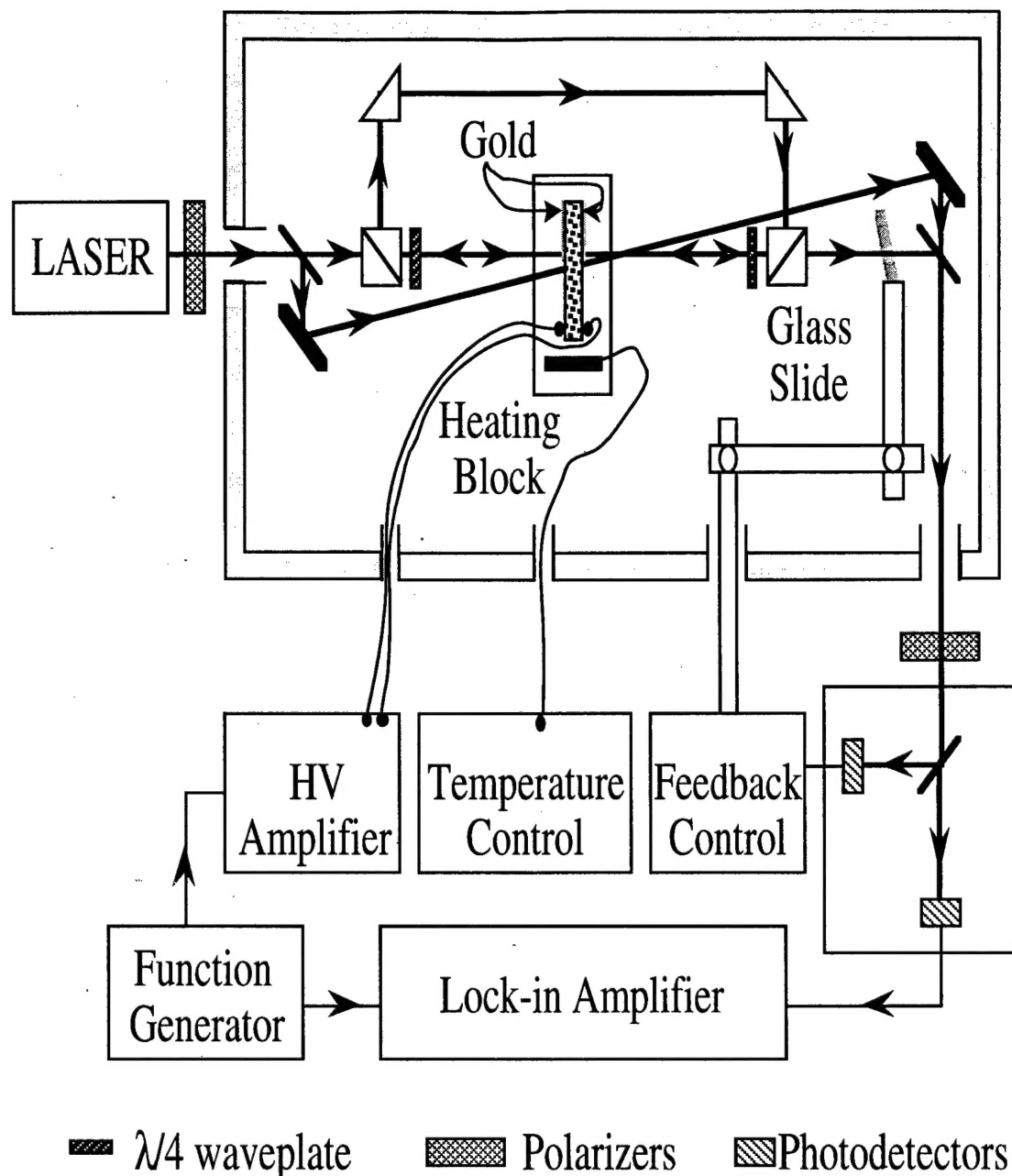


Figure 1. Modified Mach-Zehnder interferometer.

The hypothesis was that if the thickness variation is included in both beam paths (the interferometer arms) then any phase variation will effectively be due to only the index of refraction change in the film. The hypothesis was tested by applying AC field at various frequencies to a sample with no orientation order imposed on the sample, Fig. 2.

The output of the interferometer with the modification shows no mechanical resonance. The mechanical vibration resonance are not present in the compensated case because the thickness variation is present in both beam paths. If a mirror is inserted immediately in front of the gold coated sample, the mechanical resonance is present. The position of the reflector mirror

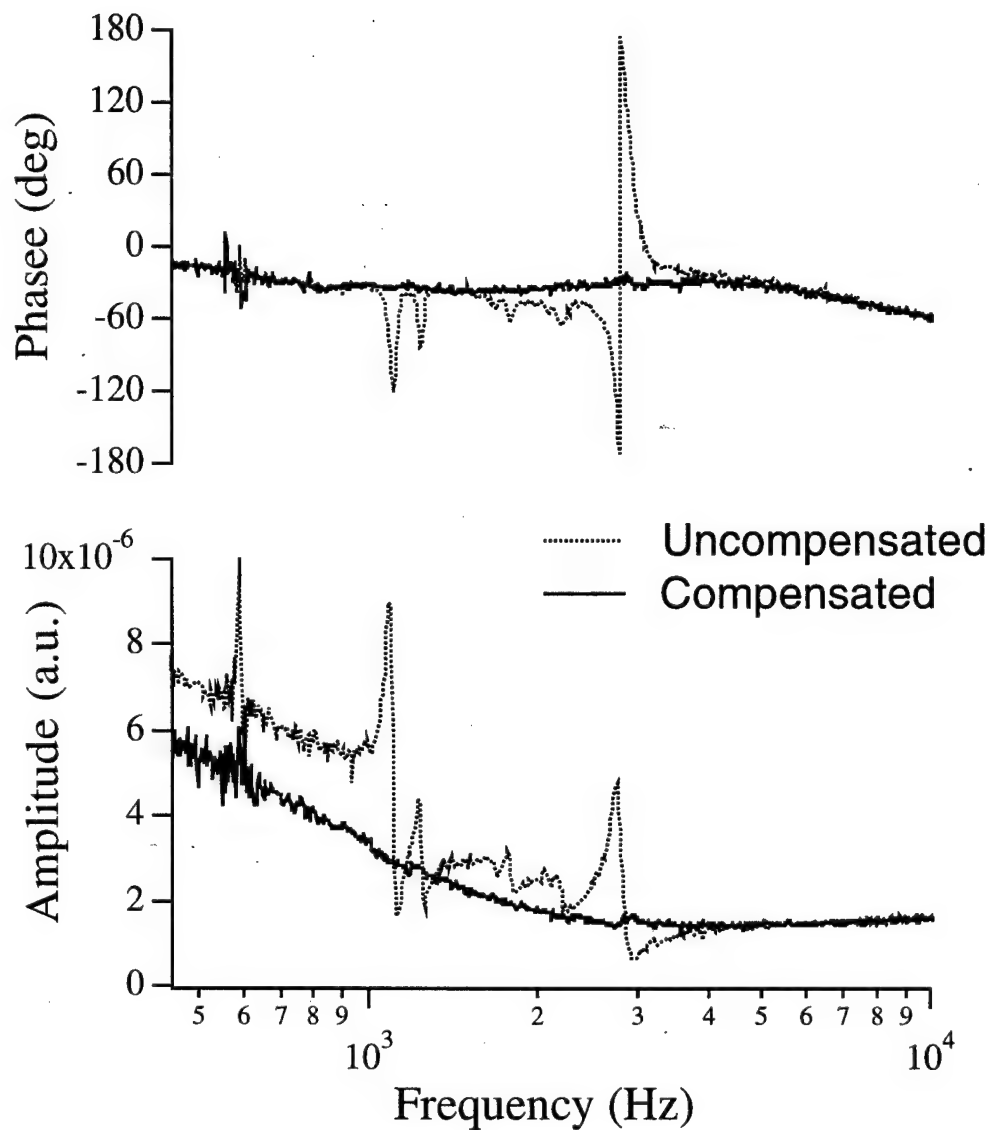


Figure 2. Effective EO coefficient as a function of frequency.

is crucial as the coherent length of the laser is very short thus the beam paths of the two arms should always remain very close.

The mechanical vibration frequency can be determined by plotting the resonance frequency verses the order of appearance. The fundamental mechanical frequency of the film is then determined from the intercept of the line. Note: this number varies with the sample holder, Fig. 3.

Figure 4 show the expected electro-optic effect with the modification. This result is now of course independent of frequency. The anomalous frequency dependence is due to the response of the voltage amplifier used. In addition, the photo diode response decreases with the increase of frequency.

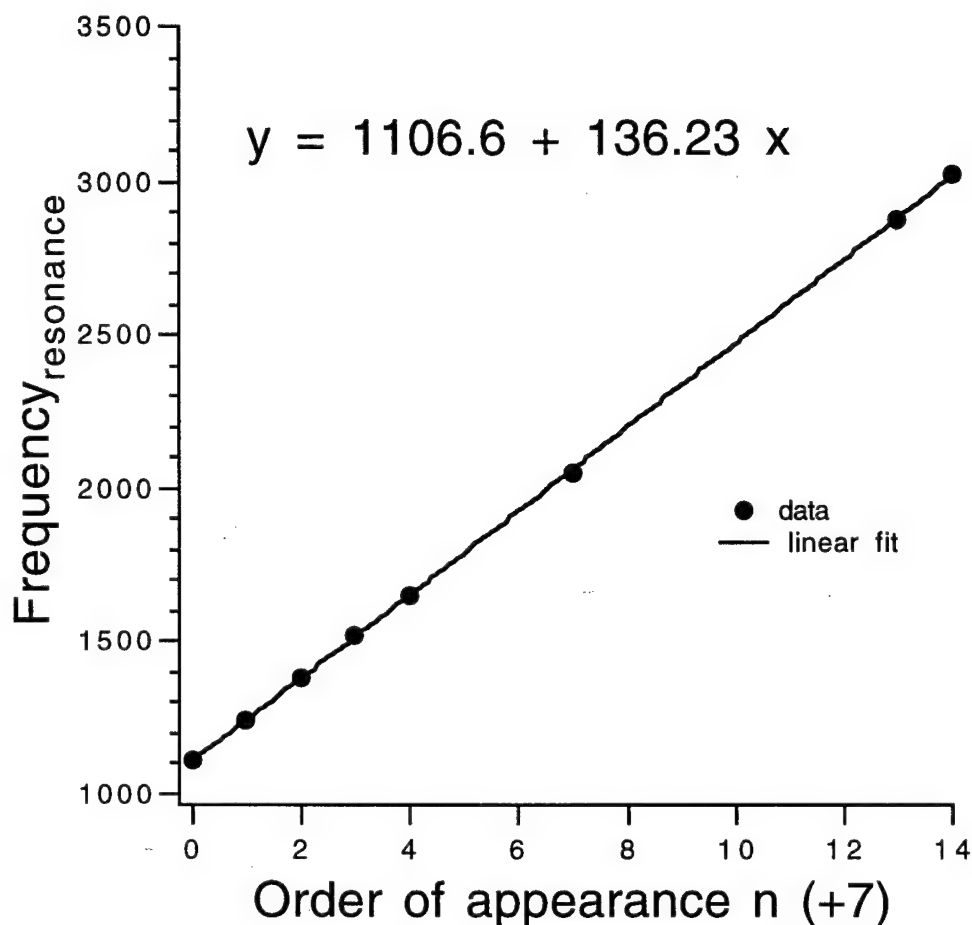


Figure 3. Determination of the fundamental mechanical vibration.

IV. CONCLUSION

The modification of the standard Mach-Zehnder interferometer incorporating *in-situ* poling made it possible to study the electro-optic effect as a function of temperature and poling field. The feed-back system incorporated in the set-up helped with the drifts due to large induced thermal variations and also with the subtle temporal drifts that plague almost all interferometers. The regulation of the interferometer intensity fluctuations to less than 0.5% for relatively long times contributed significantly to the successful reproducibility of experiments. This technique has displayed its versatility in measuring the EO effect as a function of several parameters in one experimental set-up. It was shown how this technique encompasses several experiments, by comparing the results to several independent and dispersed works. It is important to understand all the mechanical, thermal and temporal behaviors of these device oriented polymer systems before they can actually be commercially presented.

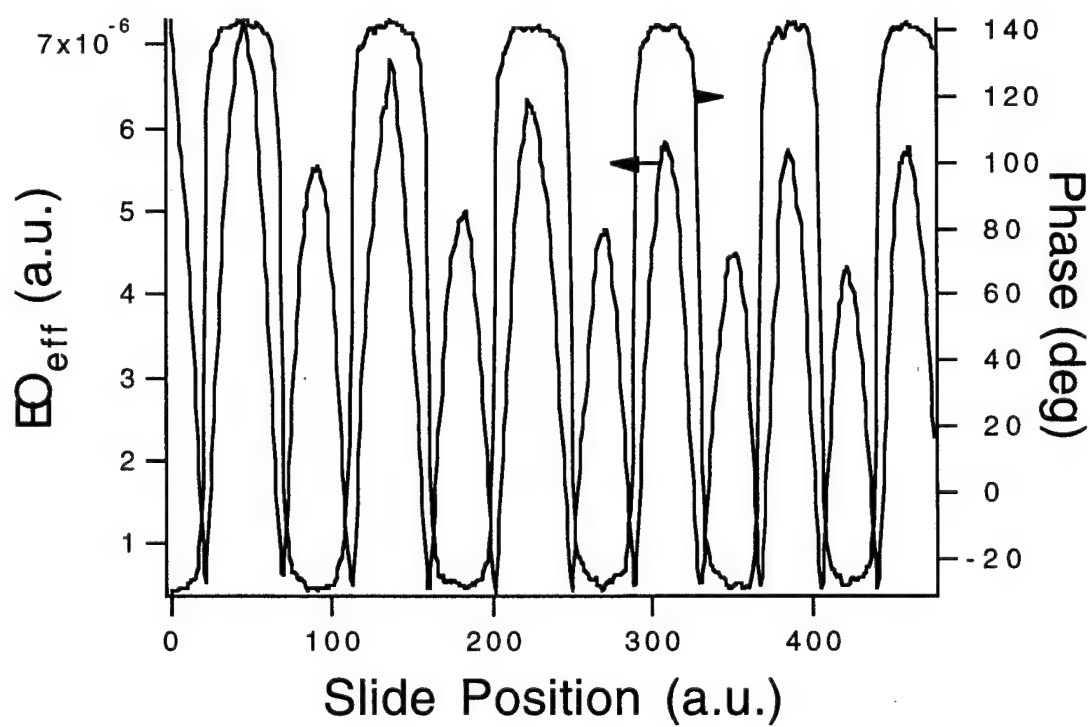
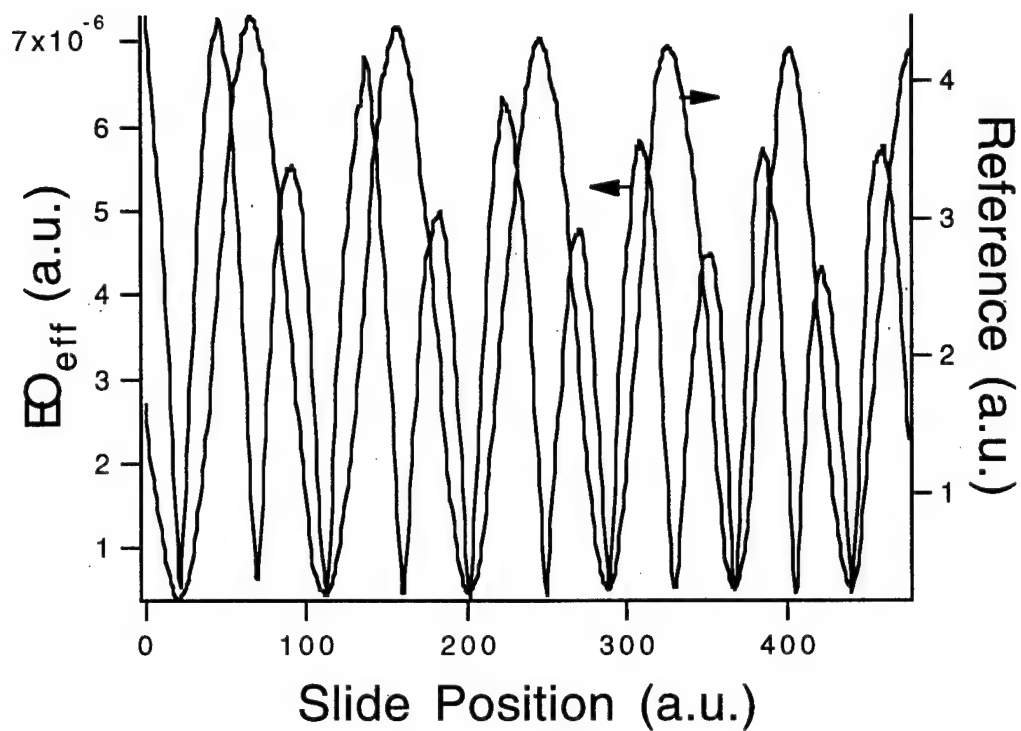


Figure 4. Effective electrooptic of 4 wt% DANS/PMMA system

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Electric Field Effects in Polymer Thin Films for Second Order Nonlinear Optical Applications

I. INTRODUCTION

The effects of large electric fields on polymer physical properties are important in many fields, including photonics, electric power transmission, and telecommunications.^{1, 2} In these areas polymers are widely used as electronic insulators in coatings and cables as well as substrates in capacitors and transformers.³ Previous research concerning electric field effects on polymers has been performed only under the conditions of electric field-induced breakdown or on bulk polymer samples.^{4, 5} Little research has been performed concerning polymer films with thicknesses less than 10 μ m. The goal of this research is to determine the charge magnitude, symmetry and distribution across polymer thin film systems for second order nonlinear optical applications as a function of time, temperature, thickness, poling and concentration of dopant. In addition, the electric field effects on the orientation of chromophores in the polymer film will also be studied. The primary techniques that will be used are electrochromism, second order nonlinear optics, dielectric relaxation, and thermal pulse measurements.

Polymer thin film systems have been explored as potential materials for optical device applications using second order nonlinear optical effects such as second harmonic generation and linear electrooptic effect.¹ Possible photonic devices such as waveguides and frequency doublers may use nonlinear optical polymer thin film systems as an active media. For second order nonlinear effects to be observed, a noncentrosymmetric orientation of the chromophores is necessary.⁶ To obtain this orientation, the polymer system may be poled with a large magnitude electric field.⁷ The effects of the electric field during and following poling are poorly understood. Therefore, to make efficient nonlinear optical devices, it is necessary to understand the electric field effects on the thermal and temporal stability of chromophore orientation within the polymer thin film system as a function of processing.

This research presents a novel approach using both electrical and optical methods to characterize the electric field effects in polymer thin films. The goals of this research can be summarized as follows:

- 1) Determine the average electric field and the polarization distribution across the polymer thin film as a function of time, temperature, thickness, poling and concentration of dopant using electrochromism, second order nonlinear optics, and thermal pulse measurements.
- 2) Determine how the applied electric field affects rotational mobility of chromophores in polymer systems using dielectric relaxation and second order nonlinear optics.

Many techniques will be used in order to accomplish these goals. The first technique is electroabsorption which will be used to determine average electric field across the polymer thin films. Thermal pulse measurements will be performed to determine charge distribution in polymer systems. These methods will characterize the electric field distribution through the polymer thin film. Dielectric relaxation measurements will be performed to determine the average relaxation time of the polymer systems. Second harmonic generation measurements will be performed to study the rotational mobility of chromophores in polymer systems. These two methods will characterize the relaxations of the polymer and the orientational stability of the chromophores in the polymer thin film systems.

This research represents an attempt to completely characterize the pivotal electric field effects in second order nonlinear optical polymer films so that practical processing methods can be developed for device manufacture and implementation. To understand the relaxation of chromophores in the polymer hosts from a poling-induced noncentrosymmetric orientation, an understanding of the electric field effects as well as the polymer physics effects is essential.

II.1. Electrochromism

Question to be answered: *What is the average electric field across the polymer film?*

Goals answered: *The average electric field through the polymer film is obtained as a function of poling and concentration of chromophore.*

Electrochromism is a change in the absorption curve of a material resulting from the application of an external DC electric field.⁸ By applying a DC field across a thin film properties of the material can be determined including the dipole moment at the ground state⁹, changes in dipole moment⁹ and polarizability¹⁰ during excitation, and the degree of orientational freedom of the chromophore in a polymer matrix.⁹ Electroabsorption is the change of the absorption of the material due to an applied AC electric field.¹¹ Electroabsorption has been used to study the electric field profiles in semiconductors^{11,12} and charge transfer transitions in polycrystalline materials.¹³⁻²⁰ In addition, the average electric field through the polymer film can be determined using this method.¹⁷

Electroabsorption is used to find the average electric field through the polymer film. The modulation of the applied electric field causes a modulation in the transmittance through the polymer thin film. The observed change of transmittance can be described by the equation:

$$\frac{\Delta D}{F^2} = A D|_{E=0} + \frac{\nu}{15h} B \frac{d(D/\nu)}{d\nu} \Big|_{E=0} + \frac{\nu}{30h^2} C \frac{d^2(D/\nu)}{d\nu^2} \Big|_{E=0} \quad (\text{II.1})$$

where D is the optical density, F is the local electric field sensed by the chromophore, ν is the optical frequency, h is Planck's constant and A , B , and C are molecular parameters related to the transition moment, change of polarizability and change of dipole moment respectively. The parameter A is found to be negligible. For normal incident light and assuming the transition moment is collinear with the change of the dipole moment, which is true for most nonlinear optical chromophores, the coefficients of B and C can be obtained. Substituting the above equation is modified to:

$$\frac{\Delta D}{F^2} = \frac{\Delta\alpha}{2h} \nu \frac{d(D/\nu)}{d\nu} \Big|_{E=0} + \frac{(\Delta\mu)^2}{6h^2} \nu \frac{d^2(D/\nu)}{d\nu^2} \Big|_{E=0} \quad (\text{II.2})$$

An ac electric field is used to modulate the absorbance of the polymer film and hence its transmittance

$$F = fF_a \cos(\Omega t) \quad F^2 = \frac{f^2 F_a^2}{2} (1 + \cos(2\Omega t)) \quad (\text{II.3})$$

where f is the local field factor. By observing the transmittance at twice the frequency of the modulated applied electric field and knowing the value of the change of dipole moment obtained from the literature, the local field factor can be obtained. The average electric field through the polymer film can then be calculated.

If a poling field is applied along with the ac electric field, then equation 3 is modified to:

$$F = fF_a \cos(\Omega t) + fF_p \quad F^2 = \frac{f^2 F_a^2}{2} (1 + \cos(2\Omega t)) + 2f^2 F_a F_p \cos(\Omega t) + f^2 F_p^2 \quad (\text{II.4})$$

However, by applying a poling field, the assumption of an isotropic orientation is no longer valid. Other terms contribute to the modulation of the transmittance. If these terms are negligible or if they can be determined, then by observing the transmittance at the same frequency and twice the frequency as of the modulated electric field, the average local field factor for a poled polymer film can be determined.

A slightly different way to look at electrochromism is to realize that it is a third order nonlinear optical effect. For $\chi(3)$ effects in an isotropic medium, there exists only 21 terms, three of which are independent. With horizontally polarized light ($E\omega$ in y -direction equal to

zero) and the applied ac electric field in the z-direction only (across the thickness of the film), only two terms survive:

$$X_{2\Omega} = \chi_{xxx}^{(3)} (E_{\omega})_x (E_{\Omega})_z^2 + \chi_{zzz}^{(3)} (E_{\omega})_z (E_{\Omega})_z^2 \quad (\text{II.5})$$

The second term is equal to zero at normal incidence. Hence these terms can be decoupled. These $\chi(3)$ effect is seen with a lock-in amplifier at 2Ω , and hence related $\Delta D 2\Omega$ determined above. These same terms exist for the poled symmetry case (∞mm). In the case of an applied ac electric field with a dc bias, the above equation (detection at 2Ω) are modified to include $\chi(4)$ terms which may appear because of the applied dc field.

$$X_{2\Omega} = \chi_{xxx}^{(3)} (E_{\omega})_x (E_{\Omega})_z^2 + \chi_{xxx}^{(4)} (E_{\omega})_x (E_{\Omega})_z^2 (E_{dc})_z + \chi_{zzz}^{(3)} (E_{\omega})_z (E_{\Omega})_z^2 + \chi_{zzz}^{(4)} (E_{\omega})_z (E_{\Omega})_z^2 (E_{dc})_z \quad (\text{II.6})$$

In addition, with the application of a dc field, new terms at a modulation frequency of Ω appear.

$$X_{\Omega} = \chi_{xxx}^{(3)} (E_{\omega})_x (E_{\Omega})_z (E_{dc})_z + \chi_{zzz}^{(3)} (E_{\omega})_z (E_{\Omega})_z (E_{dc})_z + \chi_{xxz}^{(2)} (E_{\omega})_x (E_{\Omega})_z + \chi_{zzz}^{(2)} (E_{\omega})_z (E_{\Omega})_z \quad (\text{II.7})$$

These terms are detected with the lock-in amplifier at Ω , and hence are related to $\Delta D \Omega$ determined above. A full mathematical work-up of all possible electric field combinations can be found in the Appendix.

Question to be answered: *What is the rotational dynamics of the chromophores in the polymer matrix?*

Goals answered: *Rotational mobility of the chromophores in the polymer matrix is obtained in-situ as a function of temperature, time, poling, and chromophore concentration.*

Electrochromism can also be used to obtain the rotational orientation of the chromophore. If the system is anisotropic, there is not only a quadratic dependence but also a linear dependence on the applied electric field due to the anisotropic orientation of the chromophores. This can be described by the following equation:

$$\frac{\Delta D}{F} = \frac{\Delta \mu S_1}{h} v \frac{d(D/v)}{dv} \quad (\text{II.8})$$

where

$$S_1 = \langle \cos \theta \rangle - \langle \cos^3 \theta \rangle \quad (\text{II.9})$$

which has the similar angular dependence of $\chi_{xxx}^{(2)}$ for second harmonic generation. Hence, the orientation of the chromophore within the polymer matrix can be observed as a function of time.

Once again, this electrochromic effect can be thought as a second order nonlinear optical effect. For a poled polymer film (symmetry ∞mm), there are 7 terms, four of which are independent. (For SHG, there are only three independent terms. The difference is that in the electrochromic technique, Klemann's symmetry can not be assumed since measurements are within the absorption band of the chromophore. Therefore, an extra independent term exists.)

With horizontally polarized light (E_{ω} in y-direction equal to zero) and the applied ac electric field in the z-direction only (across the thickness of the film), only two terms survive:

$$X_{\Omega} = \chi_{xxz}^{(2)} (E_{\Omega})_z (E_{\omega})_x + \chi_{zzz}^{(2)} (E_{\Omega})_z (E_{\omega})_z \quad (\text{II.10})$$

This $\chi(2)$ effect is seen with a lock-in amplifier at Ω , and its decay because of the reorientation of the chromophores can be monitored as a function of time.

II.2. Thermal Pulse Measurements

Question to be answered: *What is the charge distribution through the polymer film?*

Goals answered: *The charge distribution will be obtained for films greater than 10 μ m.*

The thermal pulse experiment involves delivering a pulse of radiant energy first to one surface of the sample then to the other surface, and measuring the thermally induced electrical response after each pulse.^{4,5} This technique has been used to study the charge profile,²¹ internal electric field,²² and polarization distribution^{23,24} in polyvinylidene fluoride as well as in polar polymer systems²⁵ and ferroelectrics.^{4,5} An extensive numerical evaluation of the results have been done using Fourier analysis.²⁶⁻²⁸ A brief description of the experiment is given below.

The electrical response measured in a thermal pulse experiment is the charge transferred from one electrode to the other around an external circuit. The charge response per unit area of a thermally pulsed sample containing a polarization distribution $P(x)$ is given by

$$\frac{q(t)}{A} = \frac{\alpha_p + \alpha_x + \alpha_e}{d} \int_0^d P(x) T(x, t) dx \quad (\text{II.11})$$

where α_p , α_x , and α_e are the temperature coefficients of the polarization, thickness and dielectric constant respectively, T is the thermal rise induced by the pulse, x is the depth from the pulsed surface, d is the thickness of the doped film and t is time.⁴ When the heat diffusion is in one direction as approximated in polymer thin films, the two complementary response expressions become

$$\frac{q_A(t)}{A} = \alpha_p a_0 B_0 + (\alpha_p + \alpha_x - \alpha_e) \sum_{n=1}^{\infty} a_n B_n \exp\left(-\frac{n^2 t}{\tau_1}\right) \quad (\text{II.12})$$

after the thermal pulse is applied to the surface $x=0$ and

$$\frac{q_K(t)}{A} = \alpha_p a_0 B_0 + (\alpha_p + \alpha_x - \alpha_e) \sum_{n=1}^{\infty} (-1)^n a_n B_n \exp\left(-\frac{n^2 t}{\tau_1}\right) \quad (\text{II.13})$$

In these equations, a_0 is proportional to the energy absorbed, B_0 is the mean polarization, a_n and B_n are coefficients of the Fourier cosine series representing the initial temperature distribution and the polarization distribution immediately after the pulse and τ_1 is the thermal relaxation time given by

$$\tau_1 = \frac{d^2}{\pi^2 K} \quad (\text{II.14})$$

where K is the thermal diffusivity.⁵ The Fourier coefficients can be determined experimentally and can be used to evaluate an approximation for the polarization by the equation

$$P(x) = B_0 + \frac{1}{a_0} \sum_{n=1}^{\infty} a_n B_n \cos\left(\frac{n\pi x}{d}\right) \quad (\text{II.15})$$

In this experiment, the charge distribution as a function of film thickness is obtained for thick polymer film ($> 10\mu\text{m}$).⁵ This result is significant in the study of electric field effects of poled chromophores in polymer films. It is important to note that this technique cannot distinguish between the space charge from the polarization gradient in the polymer thin film. The characterization of both thick and thin films is necessary to develop efficient poling techniques for doped polymer films for second order nonlinear optical device applications.

II.3. Dielectric Relaxation

Questions to be answered: *What are the bulk electric field properties such as dielectric constant and capacitance of the polymer film? In addition, what is the average relaxation time of the polymer matrix as well as the polymer transition temperatures?*

Goals answered: *The average relaxation time of the polymer is obtained as a function of time, temperature, poling and concentration of chromophore.*

Dielectric relaxation is a well-established method for studying the distribution of relaxations in polymers.²⁹⁻³¹ Many researchers have used dielectric relaxation to study nonlinear optically active doped polymer systems³²⁻³⁹ and side-chain functionalized polymer systems.^{40,41} Dielectric relaxation in these systems has been used to study the intercooperativity of polymer dopant interactions as well as the rotational mobility of dopants in a polymer system.³²⁻⁴¹ In addition, dielectric relaxation has been used in many other aspects such as to study the curing of polyimids.^{37,38,42} A brief description of the method and analysis is given below.

There are three types of polarizations that contribute to the dielectric response of a material. The polarization of interest is the orientational or dipolar motions which generally occur between 10^{-4} and 10^5 Hz in polymers.³¹ The relaxation of this polarization can be observed by measuring the dielectric dispersion. Dielectric dispersion occurs at a particular frequency region for a given polymer system because of the dynamics of chain motions involved.³¹ At any temperature, there is a particular frequency or characteristic band of frequency associated with the motion of dipoles. The real part of the dielectric constant, ϵ' , is observed to decrease with frequency in a relaxation region and the imaginary part, ϵ'' , passes through a maximum when the dispersion occurs. Both constant temperature and constant frequency experiment can be performed to characterize the dielectric response of the polymer.

The Havriliak-Negami empirical function has been extensively used to analyze the broadness and asymmetrical behavior of the dielectric loss curves in polymers.⁴³ Havriliak and Negami found that the relaxation process can be represented as the sum of two dispersions, and proposed an empirical expression to represent the data

$$\frac{\epsilon^*(\omega) - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \frac{1}{[1 + (i\omega\tau_0)^\alpha]^\beta} \quad (\text{II.16})$$

where ϵ_0 and ϵ_∞ are the relaxed and unrelaxed relative permittivities, respectively, and τ_0 is the relaxation time. In this model, α and β are able to vary between 0 and 1. The parameter α represents the width of relaxation time distribution and its value increases as the width increases, and β is correlated to the asymmetric nature of the relaxation curve. A model was developed to try to assign some physical meaning to the parameters of this equation.^{44,45} The parameter α is correlated with the intermolecular dynamics, while the product $\alpha\beta$ describes the local intramolecular dynamics of the polymer. Furthermore, α decreases in the range $1 > \alpha > 0$ as the intermolecular coupling becomes stronger, and $\alpha\beta$ decreases in the range $0.5 > \alpha\beta > 0$ with an increase of hindrance of the local segments.

The average relaxation time of the polymer is studied as a function of time, temperature, poling and concentration of chromophore. These important parameters and the rotational dynamics of the chromophore determine the temporal and thermal stability of the poling-induced noncentrosymmetric orientation of the chromophore. The stability of the orientation is important in the development of second order nonlinear optical devices.

II.4. Second Order Nonlinear Optical Measurements

Question to be answered: *What is the rotational dynamics of the chromophores in the polymer matrix?*

Goals answered: *Rotational mobility of the chromophores in the polymer matrix is obtained in-situ as a function of temperature, time, poling, and chromophore concentration.*

When modeling the poled, doped films using a free gas approximation, the poled second order susceptibility is given by⁴⁶

$$\chi_{333}^{(2)} = NF^2(\omega)F(2\omega)\beta_{zzz}\langle\cos^3\theta\rangle \quad (\text{II.17})$$

where $\langle\cos^3(\theta)\rangle$ represents the orientational averaged value. The subscript "3" refers to the direction of the poling electric field and "z" represents the axis of the molecule parallel to the molecular dipole moment. Due to the characteristics of the molecule, β_{zzz} is the predominant component of the second order hyperpolarizability tensor. The angle between the z and 3 directions is represented by θ .

Relationships between experimentally measured parameters and relative values for $\chi_{333}^{(2)}$ have been developed.⁷ Assuming no dispersion and a long coherence length relative to the thickness of the film,

$$\chi_{film}^{(2)} \approx \left(\frac{I_{film}}{I_{ref}}\right)^{\frac{1}{2}} \left(\frac{2}{\pi}\right) \left(\frac{n^3}{l^2}\right)^{\frac{1}{2}}_{film} \left(\frac{l_c^2}{n^3}\right)^{\frac{1}{2}}_{ref} \chi_{ref}^{(2)} \quad (\text{II.18})$$

where I_{film}/I_{ref} is the experimentally measured intensity ratio, l_c is the coherence length of the reference, n is the refractive index and l is the thickness of the film.

The decay of $\chi^{(2)}$ is obtained experimentally. With this data, the rotational dynamics of the chromophores in the polymer matrix is studied as a function of temperature, poling, time and concentration of chromophore. Relaxation times of the poled chromophores will be obtained as well. This experiment is unique because it measures the decay rate of the orientation of second order nonlinear optical chromophores *in-situ*. This information gives insight on the temporal and thermal orientational stability of the chromophores in poled polymer thin film systems.

II.5 Charge Transport Theories and Polymer Physics

In the study of the rotational dynamics of the chromophores for second order nonlinear applications, both electric field effects and polymer physics are important. At the transition temperatures of a polymer, the polymer physical properties can change dramatically, thus influencing both the rotational dynamics of the chromophore as well as the charge mobility through the polymer itself. Polymer physical properties have been researched extensively.^{53,54} In addition, there are two established charge transport theories, the polaron⁵⁵⁻⁵⁸ and the gaussian disorder⁵⁹⁻⁶¹ models that describe charge transport through polymer films. Experimental data obtained by time of flight measurements are not accurate enough to predict which model is accurate, if any. Tom Pasmore, a member of this research group, is performing Monte Carlo simulations on charge transport through doped polymer films. These results combined with his simulations will more accurately describe charge transport through doped polymer films, which is important in optimizing the processing method for second order nonlinear optical device applications. Polymer physics and charge transport affect the rotational dynamics of poled chromophores in polymer thin films. Both effects need to be accounted for when describing the temporal and thermal orientational stability of the chromophores for second order nonlinear optical applications.

III. PROGRESS TO DATE

A brief review of the materials used and their preparation is given first. The progress to date consists of a few experiments in electroabsorption and dielectric relaxation. All experiments have been connected to a computer to facilitate data acquisition and handling. A computer program was written with Labview software to control remotely the equipment. For each experiment, the experimental setup, results and discussion will be covered briefly.

III.1 Materials Used and Sample Preparation

The samples used in these experiments were poly methylmethacrylate (PMMA) films doped with 4-dimethylamino-4'-nitrostilbene (DANS), p-diethylaminobenzaldehyde diphenylhydrazone (DEH) or Disperse Red 1 (DR1). The films were spun using a spin coater onto conductive indium tin oxide (ITO) coated slides. They were allowed to air dry for 24 hours and then were placed under vacuum in an oven for 24 hours. Next, the temperature was slowly raised above the glass transition temperature and was kept at this temperature for 24 hours. The films were then allowed to cool slowly to room temperature. This process insured that the thermal history and any preferred orientation resulting from spinning were erased. For the electroreflection and dielectric relaxation experiments, a thin layer of gold was evaporated onto the top of the film. For the electroabsorption experiments, two films were pressed together to form an ITO/ITO sandwich configuration. This process entailed pressing two films together and placing them in an oven. The temperature was raised above the glass transition temperature to allow the polymer to intermingle.

III.2 Electroabsorption Experiment

Electroabsorption measurements were made within the absorption spectrum of the chromophores which was measured using a Spectronic Genesys 5 ultraviolet-visible (UV-Vis) spectrophotometer. A 0.1 - 1 kHz AC voltage was applied across the film to create electric fields approaching 10^6 V/cm. A collimated beam from a Hg-Xe 1 kW lamp was passed through a monochromator and transmitted through the sample. The sample was placed in a Delta Design oven. A photodiode connected to a lock-in amplifier which was phased locked to the frequency of the applied field was used to observe the reflected or transmitted beam. Another photodiode was used to measure the change in intensity, if any, of the light from the lamp which was used as a reference source. The output of both photodiodes were recorded as a function of optical wavelength. A spectrum of the sample without the applied electric field was also obtained. The electroabsorption setup is shown below.

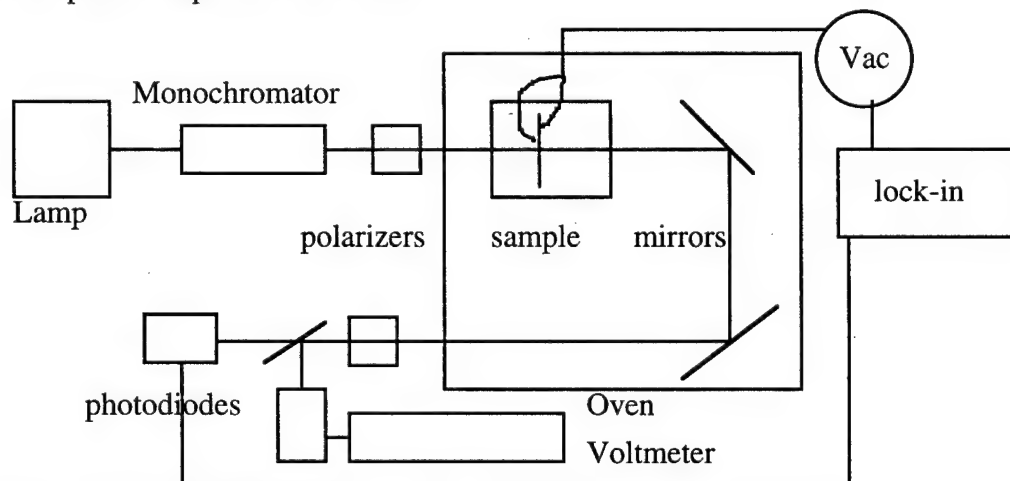


Figure 1. Electroabsorption setup.

All experimental data shown below are for PMMA + 2wt% DANS thin films. The wavelength for the experiments was 510nm, which is where optimal signal was detected. The ac field applied was 100Vpp at 1000 Hz and the dc field applied was 0V unless otherwise noted. The lamp power was set at 800W. Lastly, the angle of incidence was 0° unless otherwise noted.

The first experiment discussed is to determine if $\chi(4)$ effects are important. The $\chi(4)$ effects require noncentrosymmetric orientation, just like $\chi(2)$. Therefore, the experiment was performed at 108°C, which is above the glass transition temperature, to allow the alignment of the chromophores with the electric field. This alignment breaks the centrosymmetric orientation of the chromophores and allows even order nonlinear terms, $\chi(4)$ to exist. As shown in Figure 1, $X_{2\Omega}$ does not change with applied dc voltage.

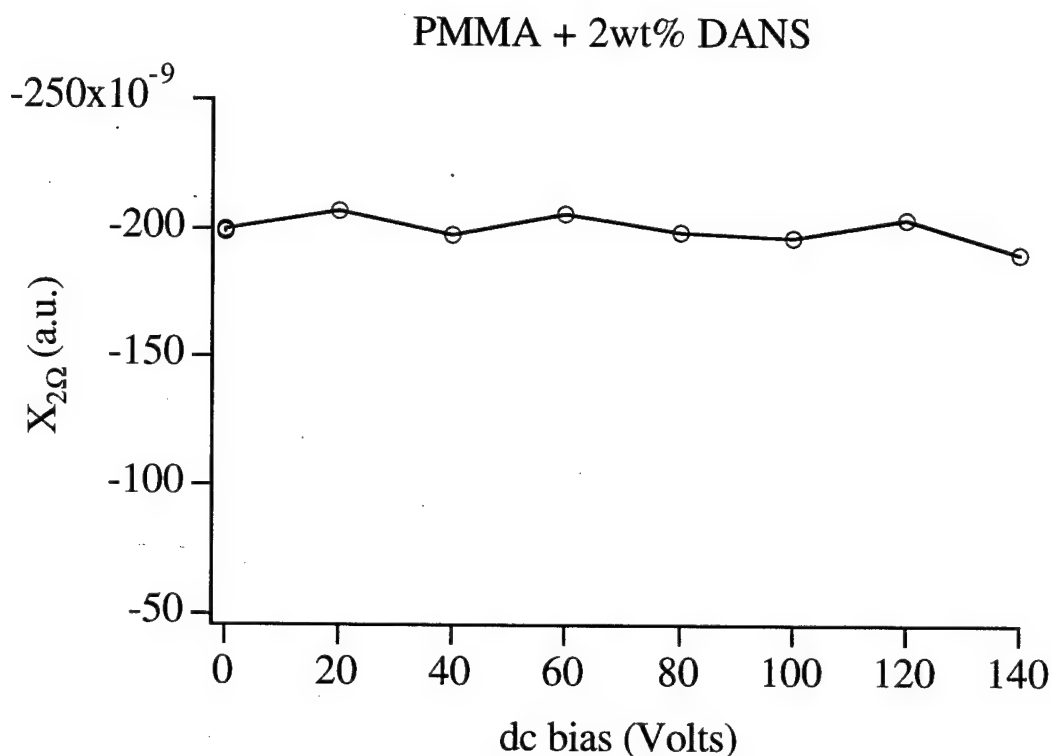


Figure 1. $X_{2\Omega}$ as a function of applied dc bias at 108°C and 20° incident angle.

If $\chi(4)$ effects were significant, a linear relationship with respect to the applied dc field would be observed as dictated by Eqn (6). A similar experiment was performed at X_{Ω} . A linear dependence with the applied dc field is expected if $\chi(4)$ effects can be neglected. As shown in Fig. 2, a linear relationship is obtained (Pearson coefficient = 0.9997). From these two experiments, it can be assumed that all terms, fourth order or higher, can be neglected. Hence all experiments performed are either $\chi(2)$, $\chi(3)$ or a combination of the two.

A frequency dependence experiment was performed, since some experiments may be performed at different frequencies. First, a chopper was used to chop the light beam at different frequencies before it passed through the sample. The signal decreased with increasing frequency because the photodiode is frequency sensitive. As the frequency is increased, photodiode sensitivity decreased. A similar experiment was performed with the application of an ac field at the same frequencies. As shown in Figure 3, the resulting response is almost the same for that of

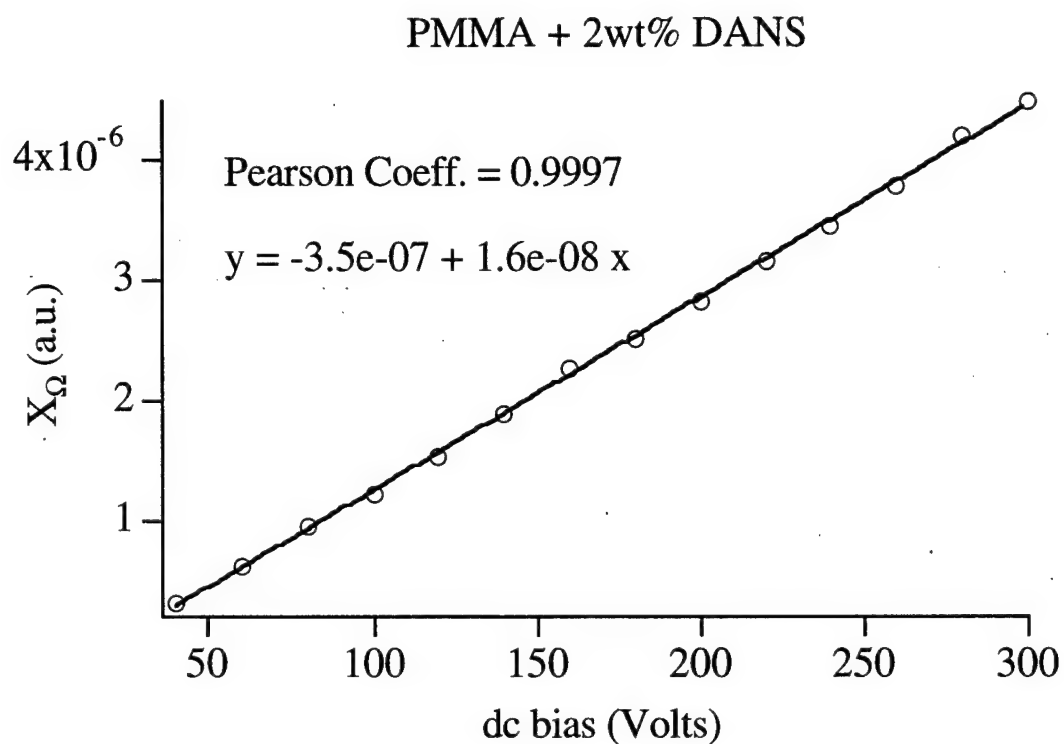


Figure 2. $X\Omega$ as a function of applied dc bias at 108°C and 20° incident angle.

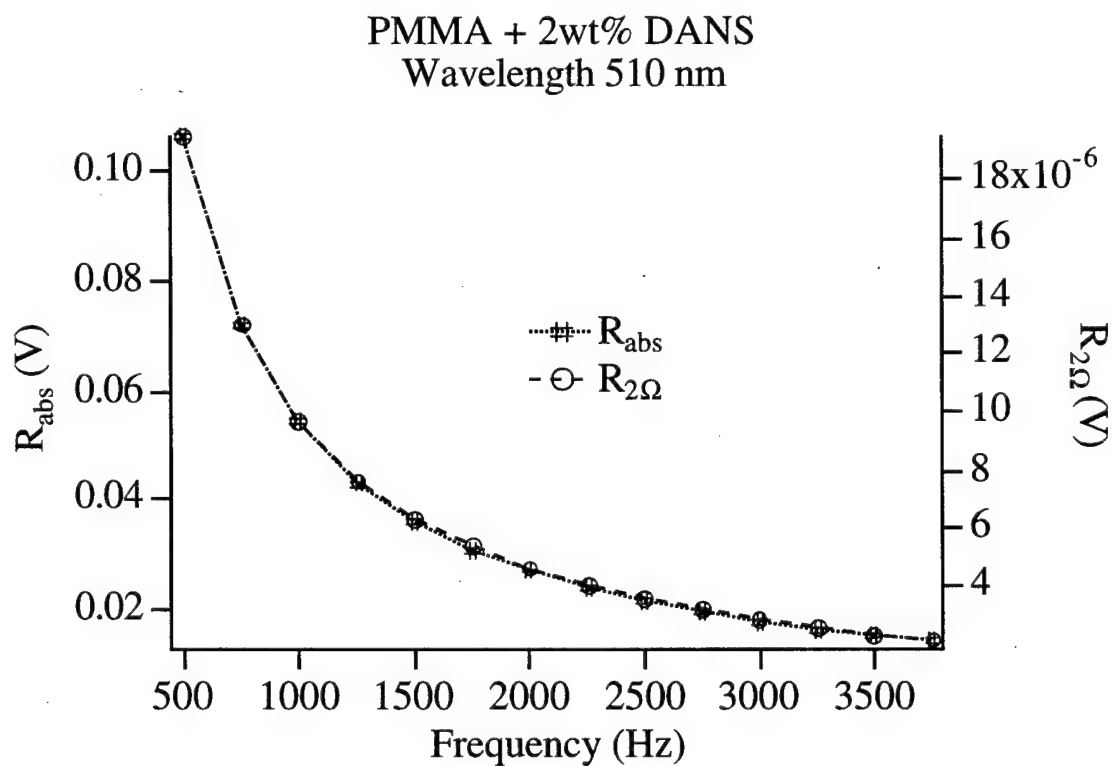


Figure 3. Frequency dependence of photodiode and of $X2\Omega$.

the photodiode. Hence, $X2\Omega$ does not depend on frequency significantly for the frequencies tested.

Since some of the experiments will be performed at different temperatures, a temperature dependence of both the optical density and the $X2\Omega$ was obtained (see Figure 4 and Figure 5, respectively). The change of optical density with temperature is important for two reasons. First, any change to the absorption spectrum will also change the derivatives of the absorption spectrum which are used to calculate the change of polarizability and dipole moment upon excitation. Secondly, a change in the optical density will change the amount of light that passes through the sample. This change will affect the intensity of the modulated light recorded by the photodiode. The change of the optical density with temperature was very small. Hence, the thermochromic effect is negligible. However, the change of $X2\Omega$ with temperature was significant. Below T_g , there was little change, but above T_g , there was a significant change in the $X2\Omega$ signal. A possible reason for this change is that the assumption of a rigid matrix is no longer valid. If the matrix is not rigid, the coefficients A and B in Eqn (1) changes. This change will affect the $X2\Omega$ signal. Hence, there is an orientation contribution to the $X2\Omega$ signal in addition to the electronic contribution. One possible application of this change of signal because of the non-rigidity of the matrix, is to measure the rotational relaxation of chromophores in polymers by measuring changes in the coefficients A and B. However, using electrochromism to measure $\chi(2)$ decay as a function of time yields the same information.

An experiment was performed to determine the difference between a poled and unpoled film with respect to $X\Omega$ signal. For an unpoled film, only $\chi(3)$ contributes to the $X\Omega$ signal. For a poled sample, both $\chi(3)$ and $\chi(2)$ contribute to the $X\Omega$ signal as described in the above

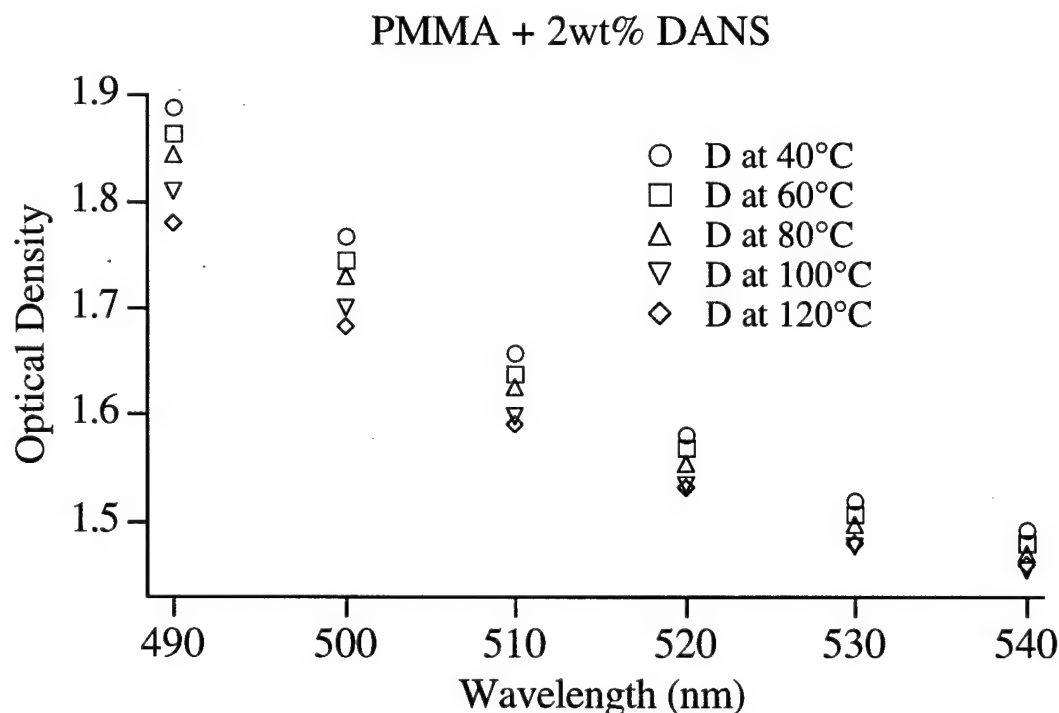


Figure 4. Optical density as a function of temperature.

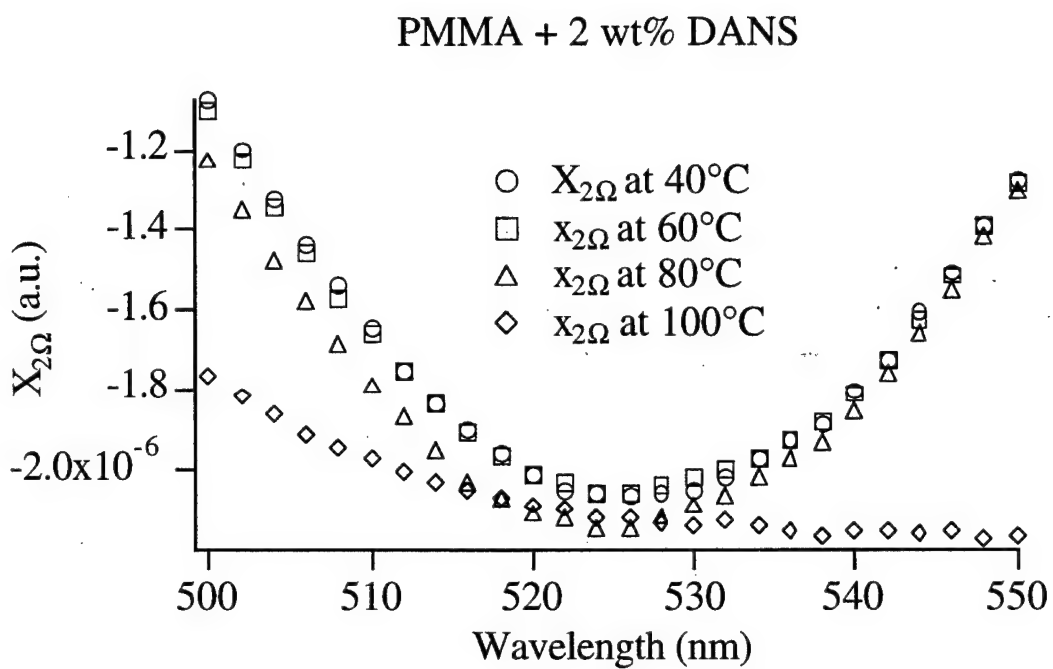


Figure 5. $X_{2\Omega}$ as a function of temperature.

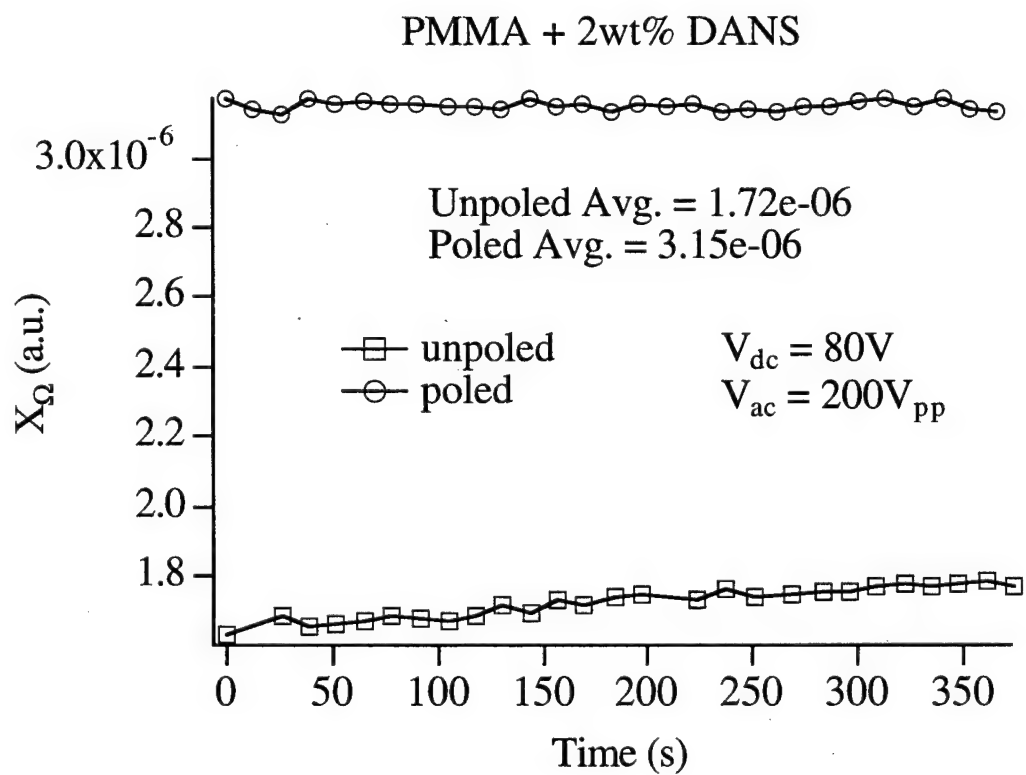


Figure 6. X_{Ω} for a poled and unpoled film.

equations. As shown in Figure 6, the poled sample signal is nearly twice that of the unpoled sample. Hence, both terms contribute significantly to the $X\Omega$ signal and neither one of the terms dominates. However, for the unpoled sample, the signal changes only slightly with time because of the poling field applied at 40°C. Hence, quick measurements of $X\Omega$ with a dc field on at low temperatures is strictly a $\chi(3)$ effect. This type of experiment can be performed to measure the extent of orientation of the chromophores which contribute to the $\chi(2)$ signal.

In addition, $X\Omega$ decay experiments were performed. $X\Omega$ is only dependent on $\chi(2)$ when there is no poling (dc) field applied. Hence, $X\Omega$ decay curves can give the same information as SHG decay curves. The parameters of the $X\Omega$ decay experiments were: wavelength was set at 510 nm; the applied ac field was 100 Vpp at 1 kHz and the incident angle was 20°. The poling temperature was 108°C, the poling time was 10 minutes, the poling voltage was 120 V and the final temperature was 80°C unless otherwise noted. The samples were raised to 108°C and kept there for 30 minutes to erase thermal history before every experiment.

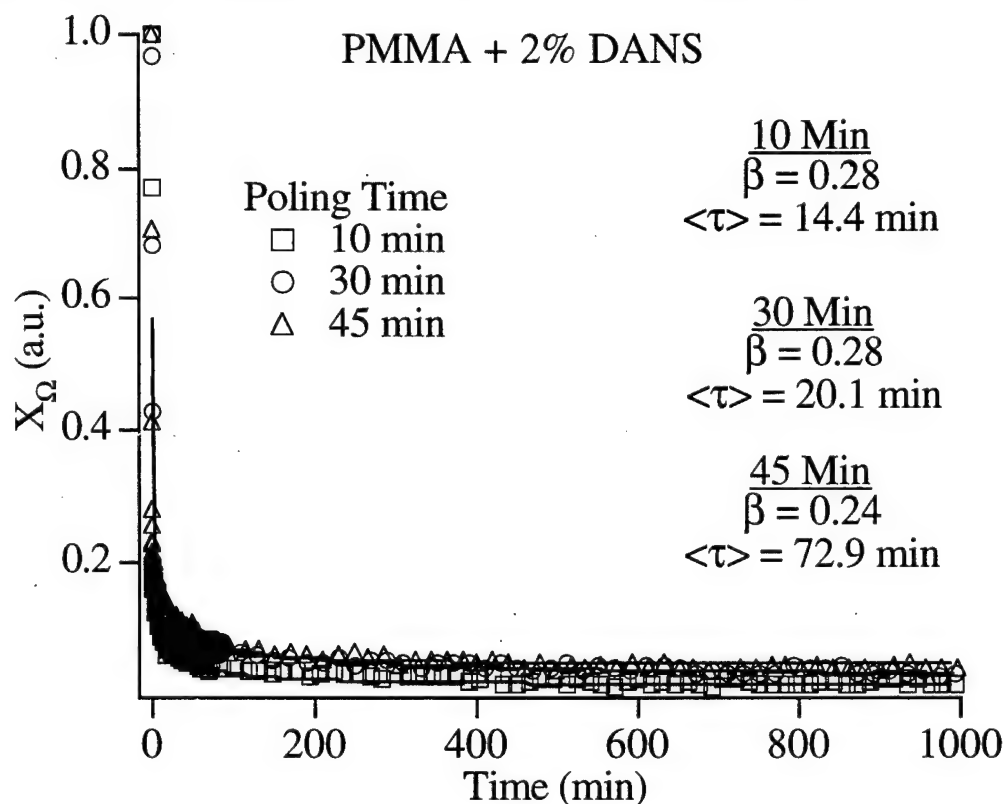


Figure 7. $X\Omega$ decay curves as a function of poling time.

$X\Omega$ decay curves were obtained as a function of poling time as shown in Figure 7. As the poling time increased the average relaxation time of the chromophores increased. With an increase in poling time, the polymer matrix has more time to equilibrate around the new chromophore orientation imposed by the electric field. An interesting observation is that β changed only slightly with an increase in poling time. This suggests that with an increase in poling time, the distribution of the relaxation times does not change much, but the entire distribution becomes shifted towards longer relaxation times. Hence, poling time does not affect the distribution of relaxation times, but only increases the average relaxation time.

In Figure 8, the $X\Omega$ decay curves as a function of final temperature are shown. As the final temperature is decreased, the average relaxation time increases dramatically and β decreases. The increase in the average relaxation time is because the polymer matrix is

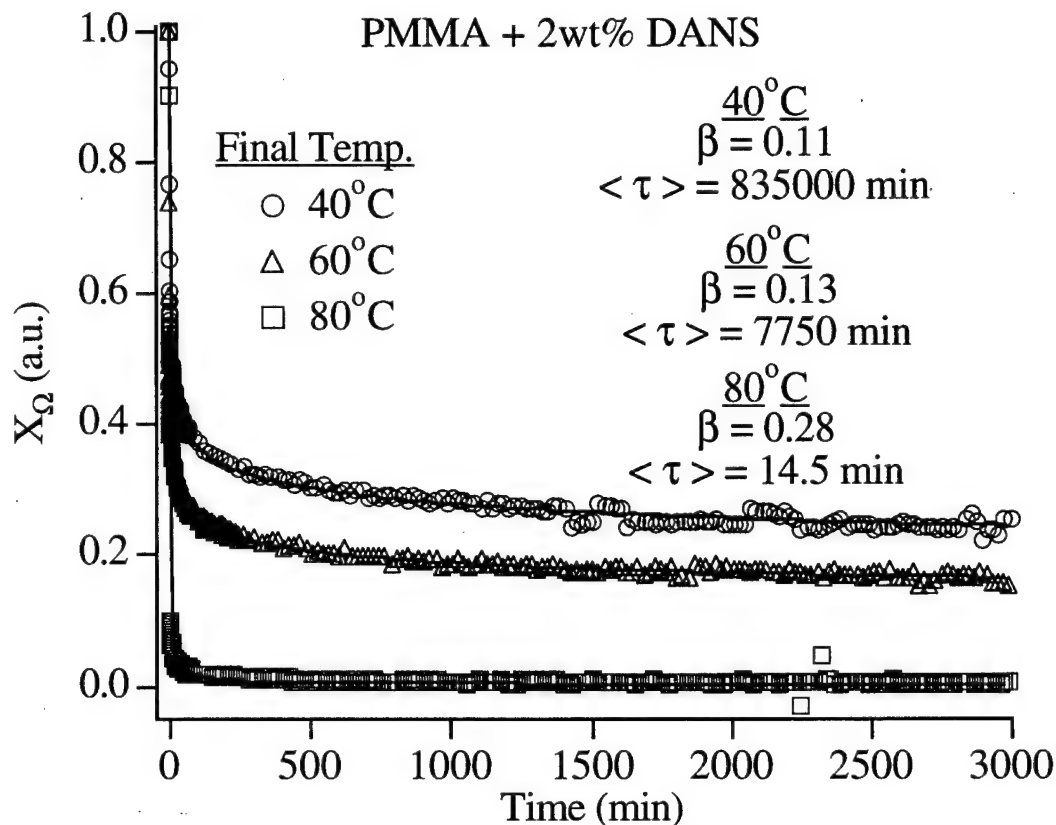


Figure 8. $X\Omega$ decay curves as a function of final temperature.

more rigid and hence restricting the chromophore reorientation. A decrease in β indicates a broader distribution of relaxation times. Therefore, a lower final temperature greatly increases the average relaxation time of the chromophores.

In Figure 9, the $X\Omega$ decay curves as a function of poling temperature are shown. The average relaxation time and b remained fairly constant as the poling temperature was varied. This shows that the distribution of relaxation times and the average relaxation time is not dependent on the poling temperature. It must be noted that all the temperatures tested were either at T_g or above T_g . Poling below T_g does not allow efficient orientation of the chromophores with the electric field because the polymer is in a glassy state which restricts the motion of the chromophores.

In conclusion, electrochromism is a versatile technique that can be used to observe both $\chi(2)$ effects and $\chi(3)$ effects in doped polymer films. This technique gives information concerning the reorientation of chromophore, $\chi(2)$ decay, as well as molecular parameters such as the local field factor.

PMMA + 2wt% DANS

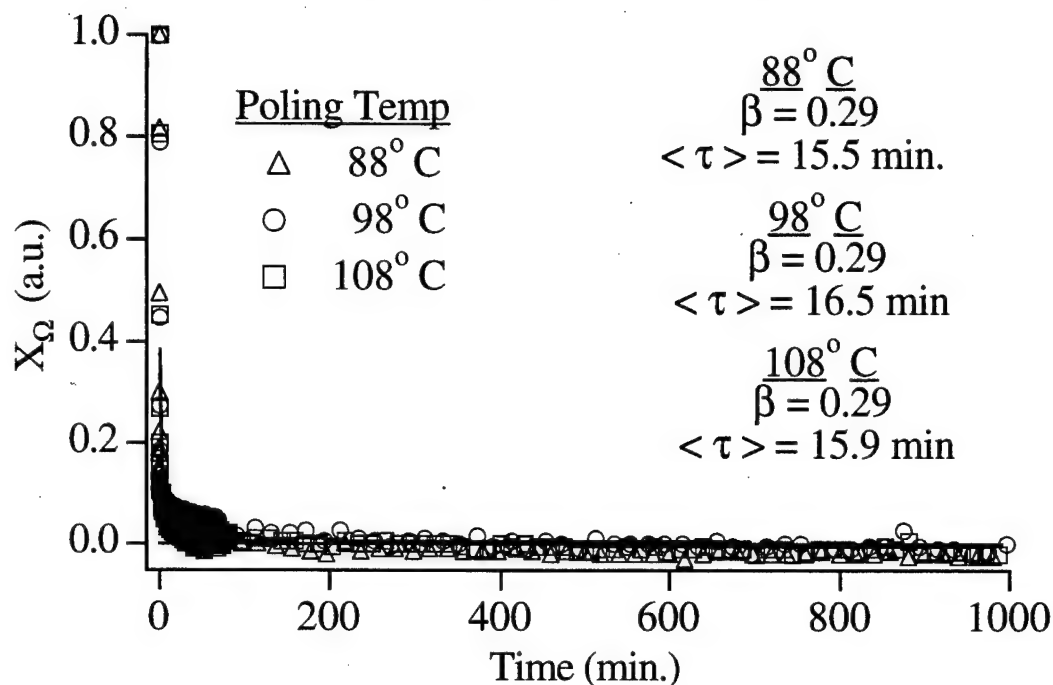


Figure 9. $X\Omega$ decay curves as a function of poling temperature.

III.3 Dielectric Relaxation Measurements

Dielectric relaxation measurements were performed using a GenRad 1689 Precision RLC dielectric bridge. The frequency range of the dielectric bridge is from 12 Hz to 100 kHz. An oven was used to control the temperature during the experiment with 0.1°C accuracy. Both the oven and the bridge were computer-controlled using LabView software.

Dielectric relaxation measurements were performed on films consisting of PMMA doped with 4 wt% DANS. The normalized dielectric loss curve as a function of normalized frequency is shown in Figure 10. These curves at different temperatures were fitted using the Havriliak-Negami equation. The results are shown in Table 1. Both α and β decrease slightly and τ decreases significantly with increasing temperature. This decrease in τ suggests an increase in intermolecular coupling. The values of α and β for 110°C does not follow the trend. Additional experiments will be performed to confirm if these results are correct. The relaxation times obtained from dielectric relaxation measurements will be used with the relaxation times from second harmonic generation experiments to determine the relaxation time as a function of temperature. The real part of the dielectric constant as a function of temperature for a few frequencies is shown in Figure 10. The dielectric constant decreases with increasing frequency. In addition, the peaks correspond to the glass transition temperature of the polymer system.

In conclusion, different concentrations of dopant as well as different dopants will be used to characterize the relaxation processes of these polymer film system used in electric field studies.

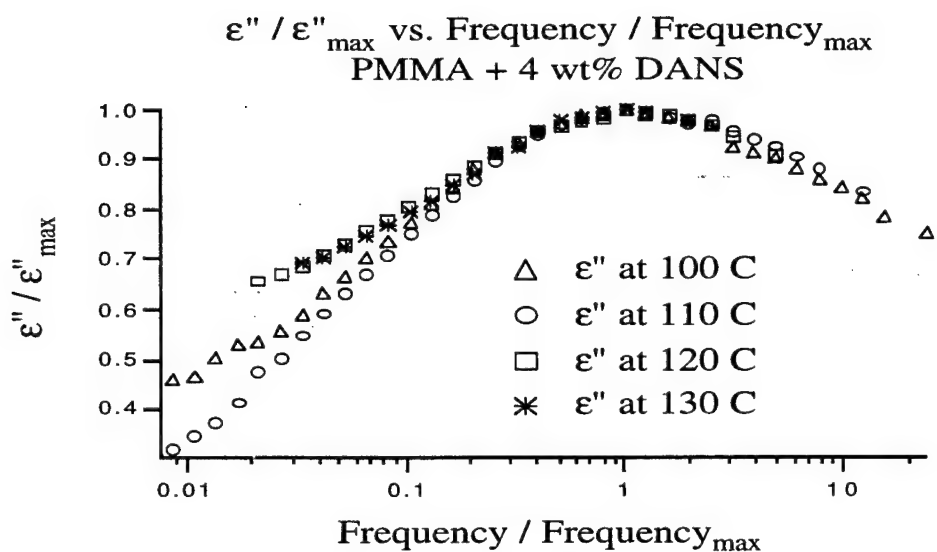


Figure 10. $\epsilon''/\epsilon''_{\max}$ vs. normalized frequency for 4 wt% DANS doped in PMMA.

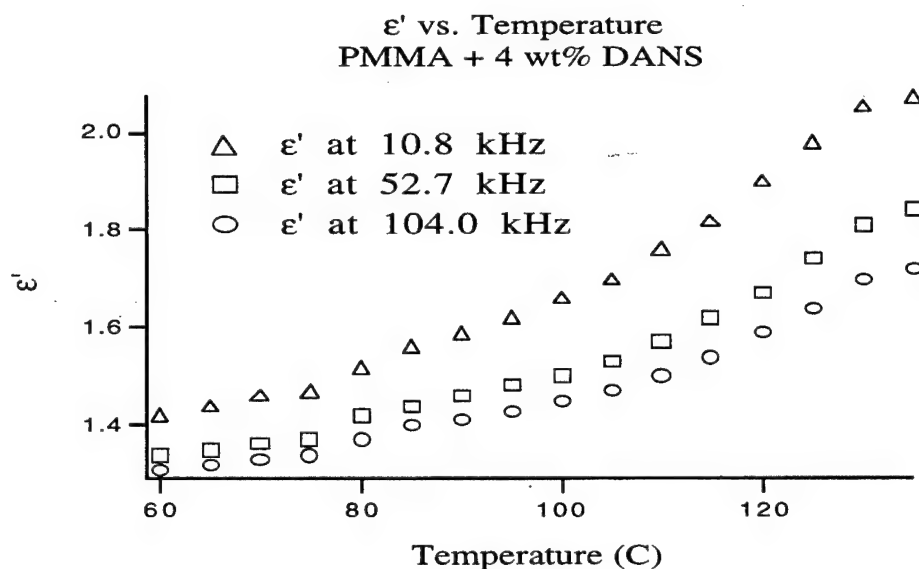


Figure 11. ϵ' vs. temperature for 4 wt% DANS doped in PMMA.

Table I. Havriliak-Negami Parameters

Temp	α	β	τ	Freq _{max}
100°C	0.38	0.99	240 μ s	3470 Hz
110°C	0.44	0.99	140 μ s	7200 Hz
120°C	0.35	0.81	70 μ s	21300 Hz
130°C	0.33	0.74	11 μ s	52700 Hz

IV. RESEARCH IN PROGRESS; RESEARCH TO CONTINUE

The proposed research will address the two primary objectives : (1) Determine the (a) charge magnitude, (b) symmetry and (c) distribution across the polymer thin film as a function of time, temperature, thickness, poling and concentration of chromophore; and (2) Determine how the electric field affects the rotational mobility of the chromophores in polymer thin film systems. In the remainder of this section detailed plans for each of these topics as well as the polymer systems that will be used will be discussed.

IV.1 Materials

The polymer systems that will be used are poly(methyl methacrylate) (PMMA), polystyrene (PS) and polycarbonate (PC) undoped or doped with 4-dimethylamino-4'-nitrostilbene (DANS), p-diethylaminobenzaldehyde diphenylhydrazone (DEH), and Disperse Red 1 (DR1). The polymers are well characterized and the dopants DANS and DR1 have been used in nonlinear optical processes. See Table II for the polymer systems that will be examined. With the PMMA systems (system 1) all concentrations and dopants will be used. Differences due to different dopants and concentrations of dopants can be observed in these systems. With the PS (system 2) and PC (system 3) systems, only DANS will be used as a dopant. Changes due to the polymer matrix can be observed and compared to that of the PMMA-DANS systems. The lower limit on concentration is 0.5 wt% because of sensitivity limitations of the techniques. The upper limit on concentration is 4.0 wt% in order to ensure that the chromophores do not aggregate. Absorption spectra of the polymer systems will be used to confirm the absence of aggregation.

IV.2 Charge Magnitude, Symmetry and Distribution

IV.2.A Charge Magnitude

The electric field that exists across the polymer thin film differs from the applied electric field because of the existence of compensation charges due to the dipolar elements in the polymer film system. The average electric field across the polymer sample can be obtained from electroabsorption as shown in Section II. Further electroabsorption experiments will be performed to obtain the average electric field across the polymer film for every system. In addition, the thermal pulse experiment will give information on the charge magnitude across the polymer film.

IV.2.B Charge Symmetry

The electric field that spans the polymer thin film may be asymmetric due to different electrodes. In addition, even if the films have the same electrodes on either side, different preferences of charge particles (either holes or electrons) may exist which will possibly cause asymmetry in the electric field. The thermal pulse experiment will give information on the surface electric field on either side of the polymer film.

IV.2.C Charge Distribution

Thermal pulse measurements will be performed at the National Institute of Standards and Technology in Gaithersburg, Maryland under the supervision of Dr. DeReggi. In this experiment, the polarization distribution or the space charge distribution as a function of film thickness is obtained for thick polymer film ($> 10\mu\text{m}$). It is important to note that this technique cannot distinguish between the space charge present in the polymer film from the polarization gradient in the polymer film. The charge distribution is significant in the study of charge mobility and rotational dynamics of poled chromophores in polymer films. The characterization of both thick and thin films is necessary to develop efficient poling techniques for doped polymer films for second order nonlinear optical device applications.

IV.3 Electric Field Effects on Rotational Mobility

The rotational dynamics of the chromophore in these polymer thin film system are important for device applications. Two methods will be used to measure the rotational dynamics of the chromophores: 1) electrochromism and 2) second harmonic generation and dielectric relaxation will be used to characterize the polymer relaxations. These methods are sensitive to different time scales; dielectric relaxation is sensitive to times under tenth of a second while second harmonic generation and electrochromism are sensitive to time scales from seconds to days.

V.3.A Dielectric Relaxation

Many parameters such as the dielectric constant and the bulk polarization in addition to the rotational mobility can be obtained from dielectric relaxation measurements. Using the Havriliak Negami empirical model, a relaxation time, τ_0 , will be obtained. The majority of dielectric experiments will be performed at temperatures above the glass transition temperature. These results will be used in conjunction with the relaxation times obtained from second harmonic generation experiments to obtain the average relaxation time as a function of temperature. Further dielectric relaxation experiments will be performed to obtain the relaxation times of the polymer film for every system.

V.3.B Second Harmonic Generation and Electrochromism

The decay of $\chi^{(2)}$ is obtained experimentally. With this data, the rotational dynamics of the chromophores in the polymer matrix is studied as a function of temperature, poling, time and concentration of chromophore. Second harmonic generation and electrochromic experiments will be performed at temperatures below the glass transition temperature. These results will be used with the dielectric relaxation results to obtain the average relaxation time as a function of temperature. This experiment is unique because it measures the decay rate of the orientation of second order nonlinear optical chromophores *in-situ*. This information gives insight on the temporal and thermal orientational stability of the chromophores in poled polymer thin film systems.

The tables below summarize the parameter that will be studied (Table II) and the techniques that will be used and the dependencies of each technique (Table III). An experimental plan of action is listed afterwards (Table IV).

Table II. Parameters

Polymer	Dopant	Conc.	Electrode	Functions
PMMA	DANS	0.5 wt%	ITO	time
PS	DR 1	1.0 wt%	Au	temp
PC	DEH	2.0 wt%		E-field
		4.0 wt%		thickness

Table III. Techniques and their dependencies.

Experiments	Dependent On	Not Dependent On
Electroabsorption	frequency, E-field	electrode, temp, thickness
Dielectric Relaxation	frequency, electrode, temp	E-field, thickness
SHG	time, temp, E-field, thickness	electrode
Thermal Pulse	time, temp, E-field, electrode, thickness	None

Table IV. Experimental Plan of Action

Experiments:

1. Electroabsorption - Experiments will be performed on all systems (1, 2, and 3) using an ITO/ITO electrode sandwich configuration. Electroabsorption measures the average electric field across the polymer thin film. This will be observed as a function of frequency and magnitude of the applied electric field. Experiments will be performed at the same temperature to negate any thermochromatic effects.
2. Dielectric Relaxation - Experiments will be performed on all systems (1, 2 and 3) using primarily an ITO/ITO sandwich configuration. Experiments will be performed with other electrodes to observe any changes due to differing work functions. Dielectric relaxation measures the rotational mobility of the polymer system. This will be observed as a function of frequency of the applied electric field and of temperature.
3. Second Harmonic Generation - Experiments will be performed on all systems (1, 2, and 3) except for PMMA/DEH systems since minimal signal would be produced. Experiments will use an ITO/ITO sandwich configuration since transmission SHG will be performed. Second harmonic generation measures the rotational mobility of the dopants in the polymer system. This will be observed as a function of time, magnitude of applied field and temperature. The effective thickness will be kept constant.
4. Thermal Pulse Measurements - Experiments will be performed on all systems (1, 2, and 3) using Al electrodes. Thermal pulse measures the polarization distribution and the space charge distribution in the polymer system. This will be observed as a function of time, magnitude of the poling electric field, temperature and thickness.

In addition to the experiments mentioned above, two other experiments are being considered. The first is a waveguiding experiment. The polymer system will be spun onto Si to make a waveguide. Waveguide modes will be excited and a refractive index profile will be obtained as a function of depth. Further details on this experiment can be found elsewhere.⁶²⁻⁶⁷ The second experiment that is being considered is a total internal reflection fluorescent spectroscopy experiment. An evanescent wave from light totally internally reflecting penetrates different depths as the angle of incidence is changed. The fluorescent lifetime of the chromophores in the polymer film can change due to an applied electric field. By measuring the fluorescent lifetime changes, an electric field distribution might be obtained. Further details of the experiment can be found elsewhere.^{68, 69}

Currently, dielectric relaxation measurements are being performed for the PMMA, PS and PC systems. Electroabsorption measurements can be currently performed as well. These experiments will be the first to be completed. The second harmonic generation experimental setup is almost completed. These experiments will be performed in the near future. Samples are prepared for the thermal pulse experiment which will be performed in the near future as well.

V. SUMMARY

This research proposes to investigate the electric field effects on polymer thin film systems for second order nonlinear optical applications. Electrochromic experiments and thermal pulse measurements will be used to obtain the electric field distribution throughout the entire polymer film system. The electric field distribution through the polymer film is important in order to optimize poling procedures for second order nonlinear optical applications. Dielectric relaxation measurements and second harmonic generation experiments will be used to obtain the rotational mobility of the chromophore in the polymer systems as a function of temperature and frequency. With a better understanding of these electric field effects, practical processing methods can be developed for second order nonlinear optical devices.

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Appendix

Mathematica Expansion of the Electric Fields

e0 = applied dc electric field (poling)

ew = light electric field

eac Cos[x] = applied ac electric field

$$\text{In}[1]:= e = ew + e0 + eac \text{ Cos}[x]$$

$$\text{In}[2]:= e^2$$

$$\text{Out}[2]= ew^2 + 2 ew e0 + e0^2 + \underline{2 eac ew \text{ Cos}[x]} + 2 eac e0 \text{ Cos}[x] + eac^2 \text{ Cos}[x]^2$$

$$\text{In}[3]:= e^3$$

$$\text{Out}[3]= ew^3 + 3 ew^2 e0 + 3 ew e0^2 + e0^3 + 3 eac ew^2 \text{ Cos}[x] +$$

$$> \underline{6 eac ew e0 \text{ Cos}[x]} + 3 eac e0^2 \text{ Cos}[x] + \underline{3 eac^2 ew \text{ Cos}[x]^2} +$$

$$> 3 eac^2 e0 \text{ Cos}[x]^2 + eac^3 \text{ Cos}[x]^3$$

$$\text{In}[4]:= e^4$$

$$\text{Out}[4]= ew^4 + 4 ew^3 e0 + 6 ew^2 e0^2 + 4 ew e0^3 + e0^4 + 4 eac ew^3 \text{ Cos}[x] +$$

$$> 12 eac ew^2 e0 \text{ Cos}[x] + \underline{12 eac^2 ew e0 \text{ Cos}[x]^2} + 4 eac^3 e0 \text{ Cos}[x]^3 +$$

$$> 6 eac^2 ew^2 \text{ Cos}[x]^2 + \underline{12 eac^2 ew e0 \text{ Cos}[x]^2} + 6 eac^2 e0^2 \text{ Cos}[x]^2 +$$

$$> 4 eac^3 ew \text{ Cos}[x]^3 + 4 eac^3 e0 \text{ Cos}[x]^3 + eac^4 \text{ Cos}[x]^4$$

Above are all the possible electric field combinations for second, third and fourth order nonlinear optical processes that can occur with a light field, an ac field and a dc field. For electrochromism, detected by a lock-in amplifier, most of these terms are not detected. The requirements for detection is that a term consists of one light field, ew, and either one or two ac fields, eac. The only terms that fit our detection requirements are in bold and underlined. Hence,

$$X_{\Omega} = 2E_{\omega}E_{ac} \cos[x] + 6E_{\omega}E_{dc}E_{ac} \cos[x] + 12E_{\omega}E_{dc}^2E_{ac} \cos[x] \quad (\text{A1})$$

$$X_{2\Omega} = 3E_{\omega}E_{ac}^2 \cos[x]^2 + 12E_{\omega}E_0E_{ac}^2 \cos[x]^2 \quad (\text{A2})$$

Equation (A1) consists of second, third and fourth order terms respectively and Eq. (A2) consists of third and fourth order terms. As discussed in the Progress To Date section, fourth order terms are found to be negligible. Therefore, $\chi(2)$ and $\chi(3)$ effects can be observed using the electrochromic technique.